Effect of Dry Grinding on Gibbsite

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(Received May 26, 1959)

The crystal structure of gibbsite, one of the aluminum-trihydroxides, is a double-layered structure, and the binding force between layers is a rather weak hydrogen bond. So, when gibbsite is ground, it is supposed that the dimension of crystal particles is reduced and the stacking disorder of layers may occur. The authors examined the structural change of ground gibbsite, and confirmed the fact that very fine gibbsite (diameter of the particles is less than 1 micron) decomposes to χ-alumina directly, and in this process boehmite is not produced. The authors also studied the thermal decomposition of ground gibbsite and checked the difference of thermal properties between unground and ground gibbsite.

Experimental

Material. — Gibbsite employed in this study is a commercial product. It consists of aggregates of small crystals of a few microns and the dimension of the aggregates is 20~30 microns. Impurities are shown in Table I.

TABLE I. IMPURITIES IN GIBBSITE

Na_2O	0.35 %
Fe_2O_3	0.009
SiO_2	0.008

Procedure. — This gibbsite was ground in a ball mill and sampled. The samples were examined by X-ray methods, including X-ray small-angle diffraction procedure, and also by differential thermal analysis (DTA). Also their ignition loss was determined.

Results

Gibbsite was ground for 100 hr., and sampled at a definite time during grinding. The ignition loss was nearly constant through this process (Table II). The result of X-ray analysis was shown in Fig. 1. It is seen from this result that

TABLE II. IGNITION LOSS OF GROUND GIBBSITE

Time of grinding	Igniton loss
0 hr.	34.4 %
1	34.4
3	34.7
6	33.9
10	34.1
20	33.7
40	34.2
100	35.0

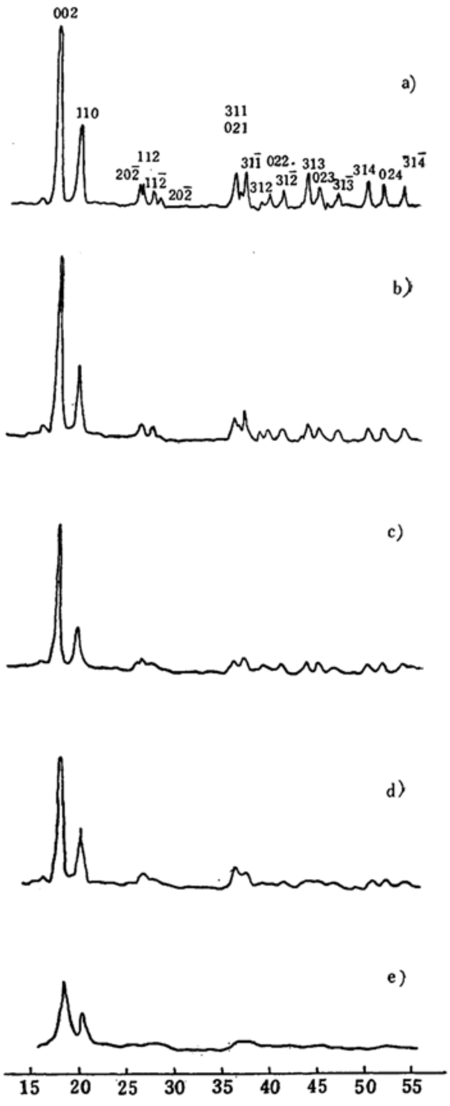

Fig. 1. X-ray diffraction diagrams of gibbsite.
a) Original gibbsite
b) Ground for 6 hr.
c) Ground for 10 hr.
d) Ground for 20 hr.
e) Ground for 100 hr.

the intensities of diffracted lines decreased gradually, and only two lines (002) and (110) were observed after 40 hr. On the contrary, the result of the small-angle scattering suffered little change (Fig. 2). From this, the authors can calculate the diameter of gibbsite by using Warren's formula[1]. Diameters of unground gibbsite and of that ground for 100 hr. are about 3500 and 2000 Å respectively. The diameter of gibbsite, ground less than 100 hr., lies between 3500 and 2000 Å. Microscopic observation reveals that an aggregate was released into some single particles, and a single particle was broken to a few fragments which have the size of about a micron. From above facts, it may be said that a particle of gibbsite which seems to be a single crystal is not continuous in the sense of X-ray crystallography. This continuous domain which is sensible for small-angle diffraction remained almost unchanged during grinding. The result of DTA was shown in Fig. 3. When the grinding time is within a few hours, ground gibbsite decomposes similarly as unground gibbsite does, that is, it reveals three endothermic peaks. But after a longer period of grinding, the DTA-curve of gibbsite changes gradually from the normal curve. The first peak becomes smaller and

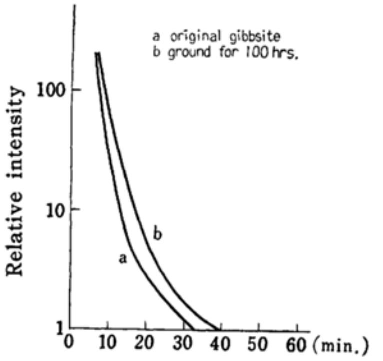

Fig. 2. X-ray small angle diffraction of gibbsite.

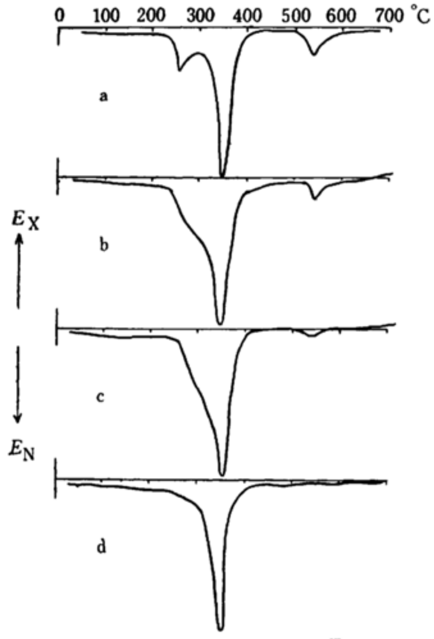

Fig. 3. DTA-curves of ground gibbsite.

a) Original gibbsite
b) Ground 6 hr.
c) Ground 20 hr.
d) Ground 40 hr.

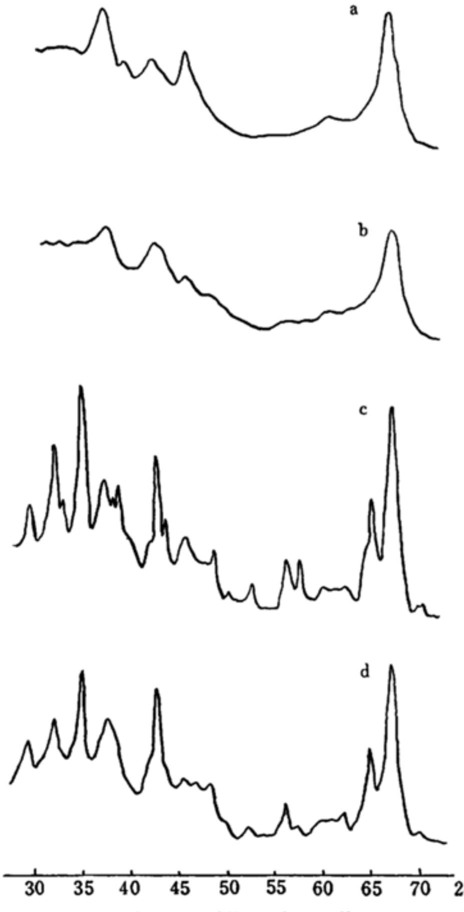

Fig. 4. X-ray diffraction diagrams of calcined gibbsite.

a) Calcined at 800°C after 3 hour-grinding [$(\chi+\gamma)$ alumina]
b) Calcined at 800°C after 20 hour-grinding (χ-alumina)
c) Calcined at 1000°C after 3 hour-grinding [$(\kappa+\theta)$ alumina]
d) Calcined at 1000°C after 20 hour-grinding (κ-alumina)

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[1] B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942).

only a knob is seen at this point. Parallel with this, the third peak becomes smaller. After the grinding of 40 hr., only the main peak is observed. This leads us to the conclusion that ground gibbsite decomposes directly into alumina; diffracted lines of alumina at 700~900°C were different from each other according to their grinding times. The diffraction of 1.99 Å became weaker and the diffraction of 2.12 Å became relatively intense (Fig. 4).

Consideration

There are many minerals, such as clay minerals, which have layered structures. In these substances the binding force within the layer is covalent and very rigid, but the interlayer force is rather weak. Lately it has been reported that there are many disordered clay minerals and theoretical calculation has been made by many authors[2].

Gibbsite, which has a composition of aluminum-trihydroxide and does not contain silicon oxide, may be said to be one of the most simple layered minerals. Therefore, it is possible to anticipate the fact that the various types of stacking along c-axis will occur in aluminum-trihydroxide. Thus it can also be anticipated that gibbsite, one of aluminum-trihydroxide-polytypes, is naturally supposed to be easily disordered by grinding. In this study, the authors can indicate that the properties of ground gibbsite are as follows: 1) gibbsite retains its composition during grinding; 2) the X-ray small-angle diffraction behavior suffers little change by grinding and appears within a very narrow range; 3) the intensities of diffracted lines become weak gradually with grinding; 4) (002) reflection does not diminish at first but becomes weak after a grinding of about 10 hr.; 5) (110) reflection still exists with (002) reflection after the disappearence of other lines.

From the facts mentioned above, it is clear that the disintegration of crystal occurred by grinding and the intensity of diffracted lines became weak. It may be said that only a slipping of layers took place so long as (002) reflection did not change, and after that the order along c-axis began to be lost with the diminution of (002) intensity. But the fact that (110) reflection remained as well as (002) after the other reflections had vanished indicates the direction of the slipping of the layers. The crystal structure of gibbsite is shown in Fig. 5 and Table III[3]. As explained already the packing of (OH) is an unusual packing of 1—2 2—1, so the direction of the slipping of layers would be [110]. In fact, it is proved that $F(110)$ is unchanged so long as the slipping of layers proceeds in the direction [110].

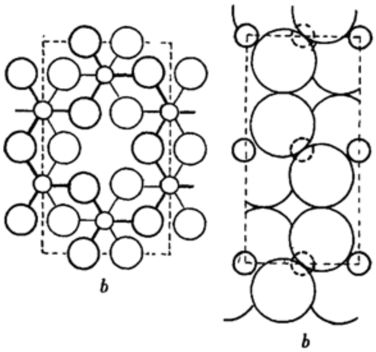

Fig. 5. Crystal structure of gibbsite.

TABLE III. CRYSTAL STRUCTURE OF GIBBSITE

Crystal class	Monoclinic
Space group	$P\ 2_1/n\ (C^5_{2h})$
Unit cell	$a=8.6236$ Å, $b=5.0602$ Å $c=9.699$ Å, $\beta=85°26'$
Z	8 $Al(OH)_3$
Atomic coordinates	$4(e)$; $\pm(X,Y,Z;\ 1/2-X,$ $Y+1/2,\ 1/2-Z)$

As seen from Fig. 5, there are two layers with a distance of $c/2$ in a unit cell and the structure within the layer is unchanged. Thus F is separated to parts F_1 and F_2, each of which is an F-factor of its own layer. Also it is assumed that a lower layer keeps its position and an upper layer slips by $\Delta r(\Delta X+\Delta Y)$. So the displacement of any atom of an upper layer is equal to Δr. Thus

$$\begin{aligned} F(110)_{\text{slipped}} &= F_1(110)+F_2(110) \\ &= \Sigma\, 2f\cdot\cos 2\pi(X+Y) \\ &\quad +\Sigma\, 2f\cdot\cos 2\pi\,[(1/2-X-\Delta X) \\ &\quad +(1/2+Y+\Delta Y)] \\ &= \Sigma\, 2f\cdot\cos 2\pi(X+Y) \\ &\quad +\Sigma\, 2f\cdot\cos 2\pi\,[(Y-X) \\ &\quad +(\Delta Y-\Delta X)] \end{aligned}$$

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[2] G. W. Brindley, "X-ray Identification and Crystal Structures of Clay Minerals", Mineralogical Society, London (1951); S. B. Hendricks and E. Teller, *J. Chem. Phys.*, **10**, 147 (1942); W. H. Zachariasen, *Phys. Rev.*, **71**, 715 (1947); C. R. Houska and B. F. Warren, *J. Appl. Phys.*, **25**, 1503 (1954).

[3] H. D. Megaw, *Z. Krist.*, **A87**, 185 (1934).

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\begin{aligned}
&= \Sigma\, 2f\cdot\cos 2\pi(X+Y) \\
&\quad + \Sigma\, 2f\cdot\cos 2\pi(Y-X) \\
&\qquad (\Delta X=\Delta Y) \\
&= F(110)_{\text{original}}
\end{aligned}
$$

In a disordered structure, the magnitude of the slipping is not constant but it is natural that (OH) of disordered gibbsite has nearly hexagonal close stacking in short range.

Many reports about the thermal decomposition of gibbsite have been published[4]. Brown and coworkers proposed the dual decomposition hypothesis of gibbsite as follows[5].

$$\begin{tikzcd}
\text{Gibbsite} \arrow[r] \arrow[d] & \chi \arrow[r] & \kappa \arrow[r] & \alpha \\
\text{Boehmite} \arrow[r] & \gamma \arrow[r] & \delta \arrow[r] & \theta \arrow[u]
\end{tikzcd}$$

Also Tertian and coworker showed that very fine gibbsite decomposed directly to χ-alumina without being contaminated with boehmite[6].

$$\text{Gibbsite} \rightarrow \chi \rightarrow \kappa \rightarrow \alpha$$

When the authors were writing this report, Dr. Tertian sent us kindly very fine gibbsite which had the diameter of about 0.5 micron. So the thermal transformation of this gibbsite was checked and, consequently, it could be recognize that Tertian's result was correct. (Fig. 6)

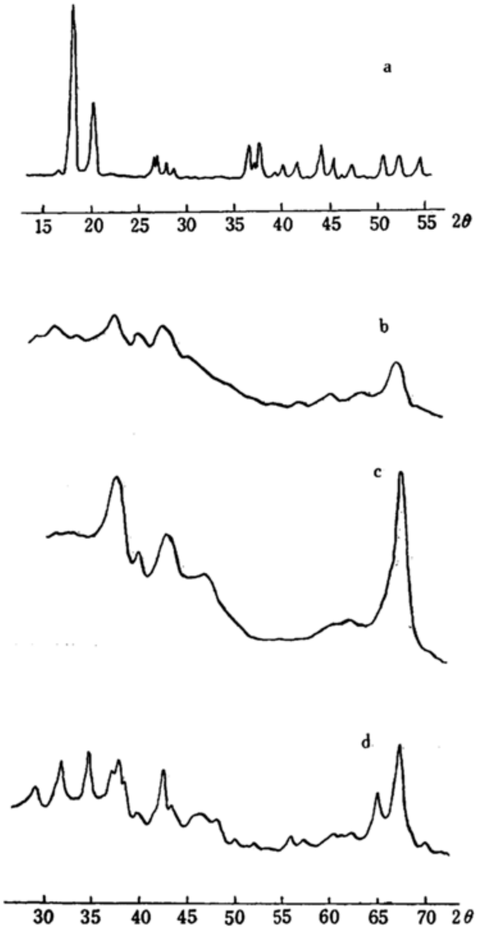

Fig. 6. X-ray diffraction diagrams of fine gibbsite.
- a) Original gibbsite
- b) Calcined at 350°C
- c) Calcined at 800°C (χ-alumina)
- d) Calcined at 1000°C (κ-alumina)

In reference to the above facts, it is expected that after long grinding, it is possible to get fine gibbsite which does not decompose into boehmite but is transformed directly into χ-alumina. The result of DTA shows that the first peak and the third peak which indicate respectively formation and decomposition of boehmite become smaller with the duration of grinding. Parallel to this, the dimension of ground crystal decreased to a micron. After 40 hr. grinding, gibbsite decomposed to alumina which did not contain boehmite. This alumina exhibited the characteristic diffraction of 2.12 Å for χ-alumina and was transformed to κ-alumina. So it may be concluded that the ground gibbsite has the same properties as the fine gibbsite. But there are some questions in this explanation. This ground gibbsite shows only two diffraction lines and is no longer true gibbsite. But it may be supposed that this gibbsite retains the essential property and structure after being ground, so the thermal property of this gibbsite would have the true character of gibbsite.

The difference of thermal property between large and small particles of gibbsite is explained as follows. When large particles of gibbsite is heated to about 200°C, the hydrothermal reaction begins to form interior crystals and dissolution of gibbsite and crystallization of boehmite occur[7]. But in the case of fine particles, the small crystal can not keep the vapor pressure in it, and the vapor evaporates, so the formation of boehmite ceases. Then the gibbsite decomposes to χ-alumina. That is, the formation

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[4] A. S. Russell et al., "Alumina Properties, Technical Paper No. 10", Aluminum Company of America, Pittsburgh, Penn. (1956).

[5] J. F. Brown et al., *J. Chem. Soc.*, **1953**, 84.

[6] R. Tertian and D. Papee, *Compt rend.*, **241**, 1575 (1955).

[7] G. Yamaguchi and K. Sakamoto, This Bulletin, **32**, 696 (1959).

of boehmite is not the result of direct decomposition but the result of hydrothermic reaction as in an autoclave, while the small particles of gibbsite can not keep the vapor pressure in it. Thus the hydrothermic reaction does not occur and boehmite is not produced from this gibbsite.

Summary

The effect of dry grinding on gibbsite was examined by X-ray diffraction, X-ray small angle diffraction and differential thermal analysis. It has been found that there are two sorts of structural change in the process of dry grinding. One, which occurs early in this process, is the slip of layers. In this stage (002) reflection retains its intensity. The other, which takes place after grinding of about 10 hr., is the three-dimensional disintegration of the crystal structure and the intensities of all diffractions become weak. Since only two reflections (002) and (110) are observed after 40 hr., it can be known that the direction of the slipping of layers is [110].

DTA-curve of gibbsite exhibits three endothermic peaks in the beginning of grinding but comes to exhibit only one peak which indicates the decomposition of gibbsite to alumina. This means that ground gibbsite decomposes directly to χ-alumina as fine gibbsite and boehmite is not produced in this process.

The authors wish to express hearty thanks to Dr. R. Tertian of Pechiney for his favor.

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